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Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 R factor = 0.057
 wR factor = 0.157
 Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

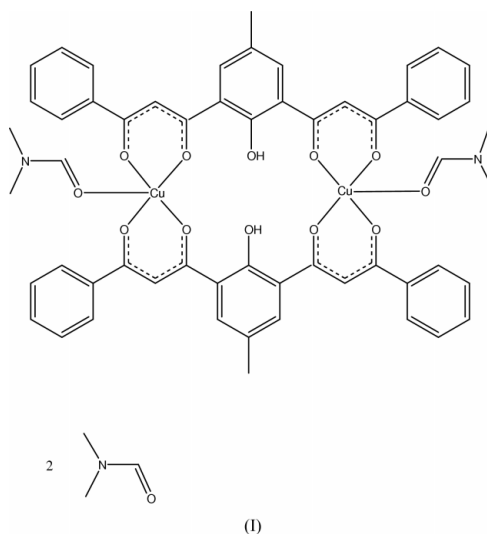
Bis[μ -2-hydroxy-5-methyl-1,3-bis(3-oxido- κ O-3-phenylprop-2-enonyl- κ O)benzene]bis(*N,N*-dimethylformamide-*O*)copper(II)] bis(*N,N*-dimethylformamide) solvate

The title compound, $[\text{Cu}_2(\text{C}_{25}\text{H}_{18}\text{O}_5)_2(\text{C}_3\text{H}_7\text{NO})_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$, is located on a crystallographic inversion centre. The bis(1,3-diketonato)phenol ligand displays a twisted conformation, with a larger planar section stabilized by an intramolecular hydrogen bond.

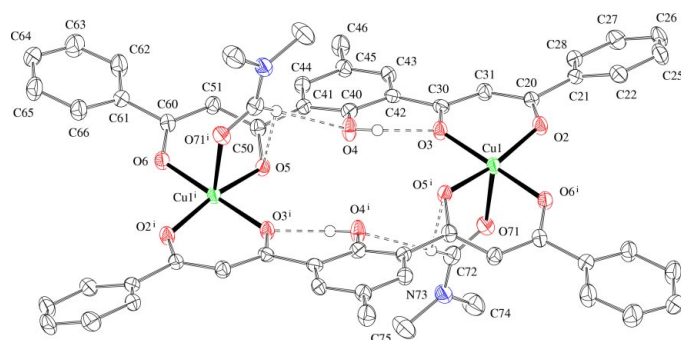
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Comment

Initial investigations on the coordination properties of the ligand 1,3-bis(3-oxo-3-phenylpropionyl)-2-hydroxy-5-methylbenzene (abbreviated H₃L) have led to a variety of coordination architectures (Aromí *et al.*, 2001; Aromí, Gamez, Roubeau, Carrero Berzal, Driessen *et al.*, 2002; Aromí, Gamez, Roubeau, Carrero Berzal, Kooijman *et al.*, 2002; Aromí, Gamez, Roubeau, Driessen *et al.*, 2002). From part of this work it was found that the preferred local stereochemistry at the metal centre in simple dinuclear complexes of formulation $[\text{M}_2(\text{HL})_2(\text{py})_4]$ (where $\text{M} = \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}$) can lead to assemblies with completely different overall structures (Aromí, Gamez, Roubeau, Carrero Berzal, Driessen *et al.*, 2002). This prompted us to determine analogous structures with different metal ions and coordinating solvents. We present here the crystal structure of $[\text{Cu}_2^{\text{II}}(\text{HL})_2(\text{dmf})_2] \cdot 2\text{dmf}$, (I).



Molecules of (I) are located on crystallographic inversion centres (see Fig. 1). The crystal contains two molecules of *N,N*-dimethylformamide cocrystallized as non-coordinating solvent for each dinuclear Cu complex. The copper ion displays a square-pyramidal coordination sphere. The Cu atom is displaced 0.1177 (3) Å from the least-squares plane through the four basal coordinating O atoms in the direction of the coordinating *N,N*-dimethylformamide molecule (all least-


Figure 1

View of the title compound, with the atom-numbering scheme. The non-coordinating *N,N*-dimethylformamide solvent molecules and H atoms not involved in hydrogen bonds have been omitted for clarity. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, 1-z$.]

squares planes mentioned in this *Comment* are calculated with unit weights). The maximum deviation of the constituent O atoms from the plane is 0.085 (3) Å. The angle between the two diketonate units coordinating to a single copper ion is 26.02 (16)°, with the diketonate moieties tilted towards the *N,N*-dimethylformamide molecule. The angles between the individual diketonate units and the basal Cu coordination plane are 14.62 (14) and 11.45 (14)° for the moieties containing O2 and O5, respectively. Owing to the inversion symmetry of the complex, the angle between the two diketonate moieties within one HL ligand is also 26.02 (16)°. The core of the HL ligand, *i.e.* without the peripheral phenyl rings, consists of two roughly planar segments, hinged at the bond C41–C50. The overall conformation of the HL ligand can be described with the angles between phenyl rings *A* (C21/C22/C25–C28), *B* (C40–C45) and *C* (C61–C66) and the diketonate moieties 1 (O2,...,O3) and 2 (O5,...,O6). The angle (*A*,1) is 17.21 (16)°, (*A*,2) is 7.76 (16)°, (*B*,2) is 33.62 (16)° and (*C*,2) 17.24 (17)°.

The OH group at O4 in the centre of the ligand HL donates a hydrogen bond to O3, thereby stabilizing the larger planar fragment of HL. Geometric details of the hydrogen bond are given in Table 2. The distance O4...O5 is significantly larger [2.673 (4) Å] than O3...O4 due to the twist of the ligand. The aldehyde H atom of the coordinated *N,N*-dimethylformamide is in quite close contact with two O atoms of the organic ligand (see Fig. 1). Details of these relatively weak C–H...O interactions are included in Table 2. The non-coordinating *N,N*-dimethylformamide solvent molecule is not involved in any weak hydrogen bonds.

Experimental

The complex $[\text{Cu}_2^{\text{II}}(\text{HL})_2(\text{dmf})_2]$ was prepared in two different ways.

Method 1: H_3L (100 mg, 0.25 mmol) was dissolved in hot EtOH (8 ml). This solution was added to a solution of $\text{Cu}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ (50 mg, 0.25 mmol) in EtOH (8 ml) and the mixture was refluxed for 1 h. A green powder was obtained, which was dissolved in DMF to saturation and layered with Et_2O . After a few days, green needles of

the title compound were obtained, which were suitable for X-ray crystallography.

Method 2: a solution of H_3L (50 mg, 0.13 mmol) in DMF (5 ml) was mixed with an equimolar amount of $\text{Cu}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ (25 mg, 0.125 mmol) in DMF (5 ml). The solution was stirred for a few minutes and was stored undisturbed at 278 K. After a few hours, a microcrystalline precipitate of the title compound had formed, which was collected by filtration. The yield was 47%.

Crystal data

$[\text{Cu}_2(\text{C}_{25}\text{H}_{18}\text{O}_5)_2(\text{C}_3\text{H}_7\text{NO})_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$

$M_r = 1216.27$

Monoclinic, $P2_1/c$

$a = 10.7840$ (10) Å

$b = 29.701$ (4) Å

$c = 8.8317$ (10) Å

$\beta = 93.015$ (10)°

$V = 2824.8$ (6) Å³

$Z = 2$

$D_x = 1.430$ Mg m⁻³

$\text{Mo K}\alpha$ radiation

Cell parameters from 537

reflections

$\theta = 2.0$ – 25.0°

$\mu = 0.83$ mm⁻¹

$T = 150$ K

Needle, green

$0.30 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector

diffractometer

φ scans, and ω scans with κ offsets

58 094 measured reflections

6483 independent reflections

4487 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.095$

$\theta_{\text{max}} = 27.5^\circ$

$h = -13 \rightarrow 13$

$k = -38 \rightarrow 38$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.157$

$S = 1.05$

6483 reflections

375 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 1.47P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.98$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.58$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–O2	1.920 (2)	O4–C40	1.347 (4)
Cu1–O3	1.918 (2)	O5–C50	1.281 (4)
Cu1–O71	2.409 (3)	O6–C60	1.287 (4)
Cu1–O5 ⁱ	1.917 (2)	C20–C31	1.407 (5)
Cu1–O6 ⁱ	1.919 (2)	C50–C51	1.407 (5)
O2–C20	1.278 (4)	C51–C60	1.396 (5)
O3–C30	1.293 (4)		
O2–Cu1–O3	91.31 (9)	O3–Cu1–O5 ⁱ	85.24 (9)
O2–Cu1–O71	96.05 (9)	O3–Cu1–O6 ⁱ	177.00 (9)
O2–Cu1–O5 ⁱ	167.60 (11)	O5 ⁱ –Cu1–O71	95.77 (9)
O2–Cu1–O6 ⁱ	90.60 (9)	O6 ⁱ –Cu1–O71	93.47 (10)
O3–Cu1–O71	88.63 (10)	O5 ⁱ –Cu1–O6 ⁱ	92.42 (9)

Symmetry code: (i) $-x, -y, 1-z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4–H4...O3	0.82	1.78	2.491 (3)	144
C72–H72...O4 ⁱ	0.93	2.48	3.382 (4)	163
C72–H72...O5 ⁱ	0.93	2.57	3.224 (4)	127

Symmetry code: (i) $-x, -y, 1-z$.

All H atoms, including the phenol H atom, were placed at calculated positions, riding on their carrier atoms during refinement. The phenol H atom was included in a position that was restricted to the plane of the phenyl ring and formed the shortest hydrogen bond.

Methyl moieties were described as rigid groups with the C atom as carrier, and were allowed to rotate around the C–C or N–C bonds. Isotropic displacement parameters of H atoms bonded to C atoms were coupled to the equivalent isotropic displacement parameter of their carrier atoms by a fixed factor of 1.5 (methyl and phenol H atoms) or 1.2 (other H atoms).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *PLATON*.

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